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Reliable Evaluation Techniques for Localized Corrosion Damages

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ABSTRACT

Reliable structural integrity assessment of a components is strongly dependent on the reliable evaluation techniques for the damages taking place on the component. Amongst the various causes of deterioration of metals and materials, corrosion is considered as one of the most dangerous culprit in raising doubt on integrity of components. Amongst the various forms of corrosion, localised corrosion is called as the silent killer of the materials. Fortunately during the last few years a number of reliable techniques have been developed who can predict exactly the extent and kinetics of corrosion taking place on a material in contact of corrodents. These techniques also help in understanding the mechanism of corrosion which is used in devising of suitable techniques to combat the corrosion and extend the life of a component. This paper incorporates the methodologies in brief on such techniques.

CAUSES OF CORROSION

Before we go in more detail on the subject, it is pertinent to discuss in brief, about certain fundamental aspects of corrosion and its control. In case of the most of the metals and materials (except certain nobler materials), their compounds are thermodynamically more stable than the parent metals. The metals, therefore, have an inherent tendency to interact with their surroundings to form stable compounds. "National Association of Corrosion Engineers" define the corrosion as a process where deterioration of metals and materials occurs due to their interaction with surrounding environments. In order that a corrosion reaction could proceed, the necessary and sufficient condition is that the formation of galvanic cells must develop at the metal/corrodent (electrolyte) interface. These galvanic cells may be macroscopic or microscopic and involve at least two reactions. One is anodic and the other is cathodic. The sites at the interface where these reactions take place are known as anodic site and cathodic site for anodic and cathodic reactions, respectively.

Anodic reactions

The corrosion of metals and alloys always takes place at the anodic sites of a metal/electrolyte interface. At the anodic sites of a corroding metal, the ionization of metal atoms into metal cations i.e oxidation takes place.

$$M \rightarrow M^{n+} + n\,e^{-} \qquad \ldots(1)$$

Metal cations are released from the metal lattices and the energy required to overcome the activation energy for dislodging the metal cations from the metal lattices is supplied from the potential developed at the metal/electrolyte interface, called potential of double layer. It is to be noted that all the metals do not release their cations from the metal lattices with equal ease. The energy required to release the cations is dependent on (a) the nature of the metal and (b) the nature of the electrolyte. These combined effects are manifested as the standard electrode potential of the metal which is defined as the potential developed at the interface of a metal in contact of its own cations maintained at 1 molar concentration at 25°C. The free energy change in the above reaction (1) i.e. ∇G is given by the equation:

$$\nabla G = -nEF \qquad \ldots(2)$$

Where, n is the number of electrons released as a result of the ionization of metal atom, E is the potential difference developed at the inetrface i.e., the electrode potential, F is the Faraday constant.

It is evident from the above equation (2) that in order to attain a negative value of free energy change the reaction (1) proceeds in right hand side, the E value i.e., the standard electrode potential of the metal should have a positive sign, where as a metal having least tendency to go into its cation, should attain the negative value of the electrode potential. Based on this principle, the metals have been arranged in a series, called electro motive force (EMF) series. In this series, where metals are arranged in an order of showing their ease with which they can transform in to their cations, are placed at the bottom portion of the series (such as Li, K, Na etc. having high positive value of EMF) where as the metals having least tendency to transform in to their cations are at the upper portion of the series (such as Au, Pt, Ag etc. having highly negative EMF values). However, if these metals are placed in the order of ease with which their cations transform into the metals, the order of the series is reversed. The corrosion engineers use the later convention of the sign and a metal least susceptible to corrosion is placed at the top (exhibit more positive potential) and a metal having highest susceptibility to corrosion is placed in the bottom (exhibit more negative potential) of the EMF series.

Cathodic reactions

In order that the spontaneity of the reaction as shown in (1) is maintained, the electrons liberated as a result of transformation of metal atoms into the metal cations, should be removed from the interface. This is achieved by the cathodic reactions i.e. the reduction of some species present in the solution/electrolyte interface. The most probable cathodic reactions that occur during the corrosion process are:

i. Reduction of a higher valance metal cations in to lower one:

$$M^{n+} + e^- \rightarrow M^{(n-1)+}$$

ii. Hydrogen evolution (generally in acidic environment):

$$2\,H^+ + 2\,e^- \rightarrow H_2$$

iii. Water/moisture decomposition in anaerobic media:

$$2\ H_2O + 2e^- \rightarrow H_2 + 2\ (OH)^-$$

iv. Oxygen reduction in alkaline or neutral media :

$$O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ (OH)^-$$

v. Oxygen reduction in acidic environment:

$$O_2 + 4\ H^+ + 4e^- \rightarrow 2H_2O$$

Thus from the above reactions, we find that for a spontaneous corrosion process, the anodic and the cathodic reactions must take place simultaneously. If any of the reaction is hindered, we observe polarization (control) of the corrosion reactions. If cathodic reaction is hindered, we call it as cathodic polarisation, where as the hindrance in anodic reaction, is termed as the anodic polarisation of the corrosion process.

Another prerequisite for the corrosion reaction to proceed is the existence of anodic and cathodic sites at the metal/electrolyte interface. Both the sites must be spatially separated but electrically connected and also should be in contact of a conducting electrolyte. As per the convention of sign of potential, as discussed previously, the anode (getting corroded) will have a more negative potential than the cathodic site (where reduction occurs). This will form a galvanic couple and the flow of current will commence. The direction of the current in a galvanic couple is from cathode to anode. The most common example of a galvanic couple is the galvanic cell comprising of Zn and Cu electrodes dipped in their respective salts and externally connected with a copper wire. The reaction proceeds at 1.1V till some hindrance (polarisation effects) are generated during the progress of the reaction.

DIFFERENT TYPES OF GALVANIC CELLS

It is clear from the above discussions that the existence of anodic and cathodic sites, reacting and conducting electrolytes are prerequisite for the onset and progress of the corrosion reactions. In other words, for a metal to corrode, the formation of galvanic cells at the metal/electrolyte interface is a prerequisite. The possible galvanic cells that cause corrosion reactions can be classified in three categories:

a. Composition cells
b. Concentration cells and
c. Stress cells

Composition cells

This type of cells are developed when two or more metals having different standard electrode potentials, come in contact with each other in conducting electrolyte. Two very popular examples are galvanized and tinned steel surfaces. If some scratch develops in these coatings, the Steel (*Eo* = -0.44V) in galvanized metal behaves as a cathode and zinc (*Eo* = -0.76V) as anode. As a result, zinc corrodes in electrolyte (humid air, water, or other conducting environments) at the cost of steel which is

protected. In case of tinned steel, on the other hand, Steel (*Eo* = -0.44V) behaves as an anode and tin (*Eo* = -0.14V) as cathode. A localized type of attack takes place on the steel surface resulting in a perforation of the structure. The other examples where onset of corrosion takes place due to the formation of compositional galvanic cells are; steel screws in brass in marine environments, propeller shafts made of steel in bronze bearings, solder of Pb-Sn on copper surface, steel pipes connected with copper plumber etc.

It is to be noted here that the galvanic cells not only form in macro level but also in micro level. Micro galvanic cells formed in two phase alloys systems are popular examples of micro cells. A steel having > 0.02% of carbon, for example, has two phases i.e cementite (Fe_3C) and ferrite. When the polished specimen of the steel is exposed to a *nital* solution, the carbide etched sample is observed microscopically, we see the darker structures of cementite (as corrosion products left on the etched cementite do not allow to reflect the light from the cementite zone).

Concentration cells

Concentration cells are formed due to the presence of two phases of electrolyte (electrolytically connected) present at the corroding interface. Formation of this type of cell can be explained by arranging a cell of a copper metal exposed in dilute solution of copper sulphate (behaves as anode) and a similar metal exposed in a concentrated solution which acts as cathode. This is obviously due to the imbalance of equilibrium existing in the solution and thus each side of copper electrode attaining different values of electrode potential. In concentration cells, therefore, a site having lower concentration of species (ions, oxygen or any other specie) behaves as anode in comparison to the site having higher concentration of the species. This aspect will be discussed in more detail in subsequent parts of the lecture.

Stress cells

The arrangement of atoms in a metal or alloy is such that they can attain the lowest energy state. However, due to certain external factors or some times due to the inherent characteristics of the metals and alloys, the atoms attain different states of energy levels and galvanic cells are developed due to the existence of potential difference. The atoms having higher energy behave as an anode where as those in lower states behave as cathode. One example is the grain boundaries in a metal or alloy, one grain has different unit and all the grains are arranged in some orientation and pattern and have same energy levels. However, at the grain boundaries, between two adjacent grains, there is a transition zone which is not aligned with other grains. If we want to see the grains structure of a metals, we can not observe it directly with microscope. The surface has to be mirror polished and then etched with a suitable etchant. These etchants attack the grain boundaries as the atoms at the grains are not at their lowest energy state and thus acquire higher negative potential (more active) and become anode. The rest of the grain, however, behaves as the cathode. This is obviously due to the stress developed at the grain boundaries during the crystallisation of metals and alloys from their molten state. The other examples of stress cell

formation is cold working of metals. An annealed wire for example when bent at a portion, due to strain hardening this portion becomes anode in comparison to the other portions of the wire and rusting of the bent portion takes place during its exposure to an electrolyte.

LOCALIZED CORROSION

As discussed earlier, for a corrosion reaction to proceed, the existence of anodic and cathodic reactions and respective sites are essential. The corrosion rate can be expressed in terms of corrosion current flowing between the anode and the cathode. It is important to note here that although, the total anodic and the cathodic currents are same but current densities (current per unit area) at the anode and the cathode may differ to a significant extent. The current density depends upon the area of anode and cathode. If area ratio between cathode and anode of a metal undergoing corrosion is very high, a localized type of attack takes place at the anode. This is owing to the fact that the total anodic current which is equal to the reduction of larger amount of species available at comparatively larger cathodic area, is produced from the smaller area of anode. Thus the current density at the anode is extremely high and causes a localized penetrating type of attack on the metal surface. This is the main cause of localized attack. Some examples of localized attack are:

Grain boundary attack

Due to small anodic area of grain boundary in comparison to grains.

Propagation of cracks

Due to very small area of crack tip (anode) in comparison to adjacent surface (cathode).

Pitting attack at the inclusions

The inclusions in metals especially sulphide types, have high electronic conductivity and encourage the adsorption of chloride or other aggressive ions on them. These inclusions dissolve as anode where as the metal matrix behaves as cathode (higher surface area). As a result, a localized type of attack takes place at the sites of these inclusions.

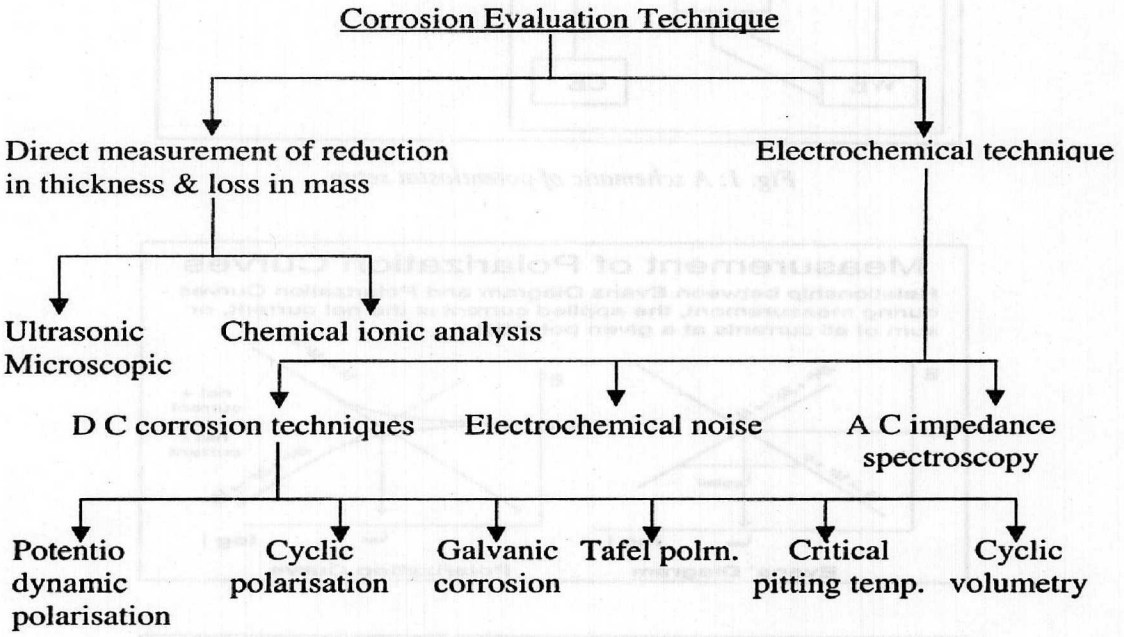
Pitting corrosion

Pitting is a form of localized corrosion and is encountered most often in technologically important metallic materials. It has been established that almost all catastrophic corrosion failures of components take place due to the onset of pit nucleation followed by the other forms of failures. Ironically, pitting is a detrimental side effect of the beneficial phenomenon of passivity.

TECHNIQUES TO EVALUATE AND UNDERSTAND CORROSION

The most commonly used method is to measure the mass loss and reduction in thickness of a component. However, these techniques are quite time consuming and

also destructive in nature. Since corrosion is an electrochemical process, the techniques based on electrochemical principles are perhaps, the most reliable and quick technique to determine the kinetics and mechanism of corrosion. These techniques can be classified as follows:



ELECTROCHEMICAL METHODS TO EVALUATE CORROSION

D C Corrosion Technique

Corrosion rate measurement by D C (Direct Current) methods usually involve applying a small amplitude d.c.signal, of either voltage or current, to a corroding metal. The resultant current or voltage, respectively is measured. The ratio of voltage to current gives resistance which is known as polarisation resistance. This resistance is usually inversely proportional to the corrosion rate.

Polarisation curves measurement

For this we need a potentiostat to control potential and monitor current and three electrodes i.e. working electrode which is a sample of interest, a reference electrode to measure the potential and a counter inert electrode for the passage of current. The arrangement for the study is shown in Figure 1.

The software available with the instrument automatically calculates the current densities produced at different potentials. We get a plot of log current density vs potential as shown in Figure 2. These plots help in determination of corrosion rate and also provide clue about the mechanism of the corrosion.

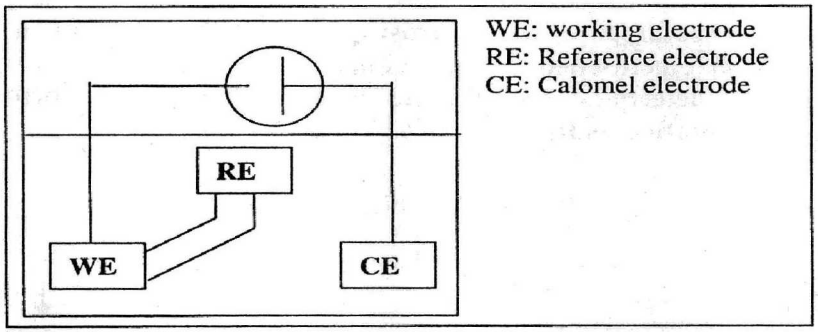


Fig. 1: A schematic of potentiostat setup.

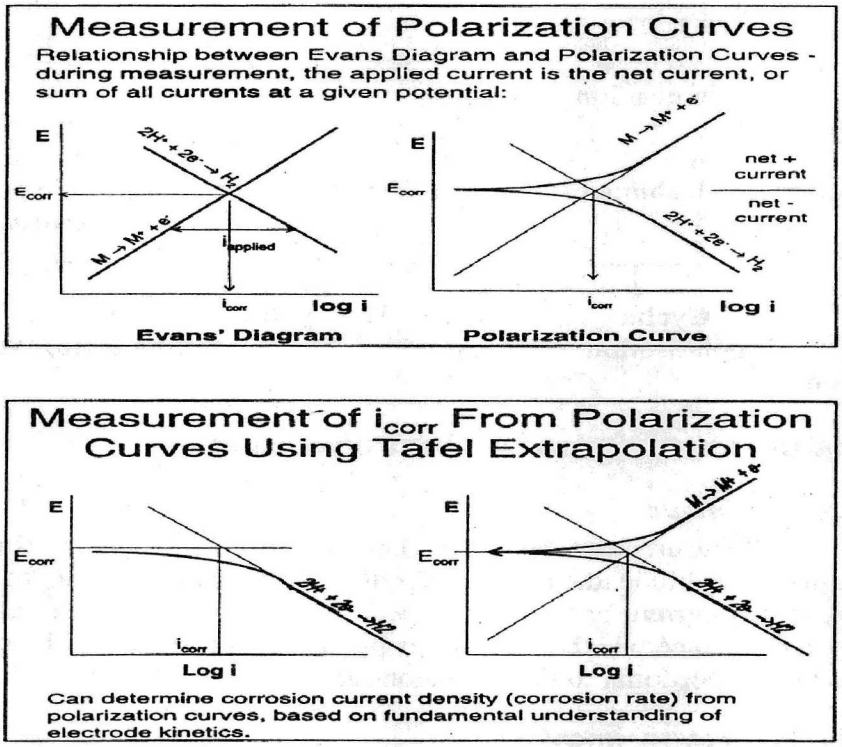


Fig. 2: Schematic of polarisation curves and method of Tafel extrapolation.

Polarisation resistance measurement

As described above the polarisation resistance of a corroding metal is inversely proportional to the corrosion rate. It was shown by Stearn and Geary that near to the corrosion potential, the polarisation resistance i.e., *Rp* is related to corrosion current (*I*corr) by a relationship:

$$I\text{corr} = \frac{ba.bc}{2.3(ba + bc)Rp}$$

Where *ba* and *bc* are the anodic and cathodic Tafel slopes respectively. *Ba* and *bc* are evaluated by polarisation diagram as shown in Figure 2 where as *Rp* is evaluated from the slope of polarisation diagram plotted in the range of ± 15-20mv.

GALVANIC CORROSION

This form of corrosion is very important from the view point of longevity of any structure corroding in an electrolyte. The galvanic corrosion of metals and alloys can take place due to various reasons. However, the most common type of problem is related to contact of dis-similar type of metals in electrical as well as electrolytic contacts. In this case, a metal which is less anodic (cathodic) corrodes slower than a more anodic metal. The very popular example is the galvanic corrosion of carbon steel pipe soldered to copper pipe where steel gets very heavy corrosion. In a galvanic series (Figure 3), the metals situated at the upper end corrode at a slower rate than the metals situated in lower part of the series. Cathode to anode area ratio is extremely important in determining the severity of the attack. In a corrosion process, if anodic and cathodic current densities are i_a and i_c and their respective electrode areas are *Aa* and *Ac*, then according to the principle of charge conservation, the total anodic current will be equal to the total cathodic current, i.e.,

$$i_a Aa = i_c .Ac$$

$$\text{or } i_a = i_c .Ac/Aa$$

Thus if *Ac/Aa* i.e., the area ratio of cathode to anode is very high, the resultant anodic current density will also be very high. This will result in very high rate of dissolution of active metal. To minimize the effect of corrosion, *Ac/Aa* should be maintained minimal.

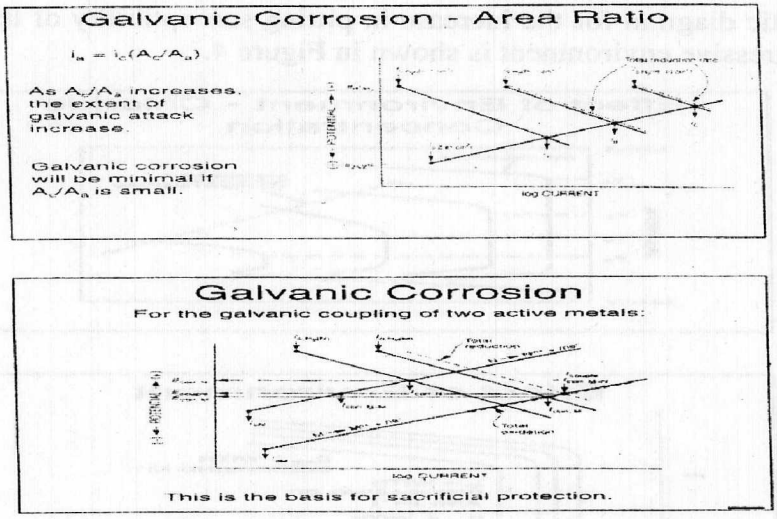


Fig. 3: Effect of anode to cathode ratio on galvanic corrosion.

ALTERNATING CURRENT IMPEDANCE STUDIES (ACI)

There are certain disadvantages associated with DC Corrosion polarisation resistance technique in determining the corrosion rate of metals. The most negative aspect is that this technique needs the polarisation of the electrode at ± 20mv of its corrosion potential. The disturbance of the interface at such a high value of potential interferes with the double layer formed at the corroding metal/electrolyte interface and affects the actual rate of corrosion. To overcome this proble ACI techniques have been developed. This technique requires the imposition of about 5 mv of A/C voltage at the interface at higher to low frequency (normally kHz to μHz) and resultant response from the interface is recorded. The data is analysed by using different models to determine the polarisation resistance and charge transfer resistance. This technique is quite useful for painted surface and to the metals forming very stable passive film as well as to the elctrolytes having very poor conductivities. The technique is also useful in determination of mechanism of corrosion.

DETERMINATION OF PITTING SUSCEPTIBILITY OF A MATERIAL

As described above, the pitting is an offshoot of defective protection. If a metal/alloy forms passive layer, the susceptibility to pitting of that metal/alloy is maximum. Similarly if large portion of the corroding surface is protected, the small unprotected portion is very susceptible to corrosion. To determine the susceptibility to pitting corrosion, only electrochemical techniques are rated to be the most appropriate. Some of these techniques are described below:

DC cyclic polarisation technique

The schematic diagram for the increase in pitting susceptibility of the material with increase in aggressive environment is shown in Figure 4.

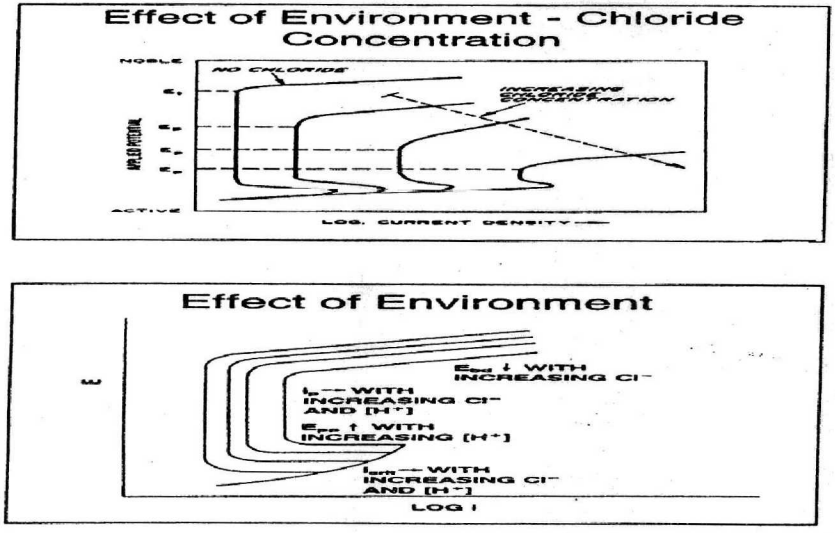


Fig. 4: Effect of chloride ion concentration on anodic polarisation.

An indication of the susceptibility to initiation of localized corrosion in this test method is given by the potential at which the anodic current increases rapidly. The more noble this potential, obtained at a fixed scan rate in this test, the less susceptible is the alloy to initiation of localized corrosion. The results of this test are not useful to correlate in a quantitative manner with the rate of propagation that one might observe in service when localized corrosion occurs. In general, once initiated, localized corrosion can propagate at some potential more electropositive than that at which the hysteresis loop is completed. In this test method, the potential at which the hysteresis loop is determined at a fixed scan rate. In these cases, the more electropositive the potential at which the hysteresis loop is completed the less likely it is that localized corrosion will occur.

Electrochemical noise

In this technique, we are not concerned with audible sounds but with fluctuations in electrochemical potential and current. Thus the electrochemical potential noise is the fluctuation in the electrochemical potential of an electrode relative to a reference electrode. Where as electrochemical current noise is the fluctuation in an electrochemical current. To measure the electrochemical noise, the electrodes undergoing corrosion are monitored for their change in current and potential with time. This is known as the electrochemical noise time record.

Electrochemical noise is the electrochemical method with the best prospect of detecting and monitoring localized corrosion processes such as pitting, crevice corrosion and SCC (although this is more a statement that other methods do not work than that electrochemical noise does). A considerable amount of work has been done to evaluate electrochemical noise for this purpose, but the best analysis methods remain somewhat uncertain. Localized corrosion is generally associated with larger electrochemical events than uniform corrosion. For example, an electrode undergoing pitting corrosion frequently displays characteristics current transients that are associated with the initiation, growth and repassivation of metastable pits (Figure 5).

Hence methods used to detect localized corrosion are generally concerned with the identification of large amplitude events. One obvious way of doing this is to look at the time record; the human visual cortex provides an extremely powerful pattern recognition tool, and one that we have difficulty in emulating with mere mathematics. However, visual examination suffers from a severe boredom factor, and analytical methods of identifying localized corrosion are needed to allow the technique to be used for routine corrosion monitoring.

Identification and examination of pits

Although this aspect is extremely covered under ASTM G46-94, however, for the benefits of the readers and for ready reference a brief write-up on this aspect will be described here.

Visual inspection: This is the simplest way of finding the pitting on a corroded surface by naked eye. In this technique a low power magnifying glass can be used.

The corroded surface is often photographed before cleaning of the corrosion product to compare the surfaces. The composition of the corrosion product helps in to determine the causes of pitting.

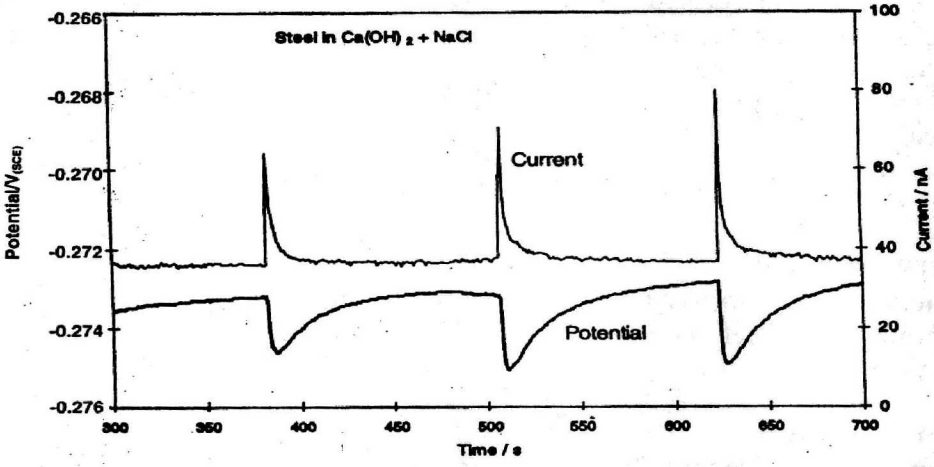


Fig. 5: Current and potential transient associated with growth and repassivation of metastable pits.

Metallographic technique: This helps in to find out the causes of pitting and establish the correlation between inclusion and pitting. The morphology of the pits also help in to know whether the pit is formed due to the electrochemical corrosion or due to dropout of metal, intergranular corrosion or due to dealloying.

Radiography: This is a non-destructive technique for knowing the damage of the equipment caused due to pitting. In this technique, radiation such as x-rays, are passed through the object. The intensity of the emergent rays varies with the thickness of the material. This technique is least useful in detection of pitting but very useful for comparing the materials susceptibility to pitting after exposure to a corrosive environment.

Electromagnetic technique: Eddy currents can be used to detect defects or irregularities in the structure of electrically conducting materials. When a specimen is exposed to a varying magnetic field, produced by connecting an alternating current to a coil, eddy currents are induced in the specimen, and they in turn produce a magnetic field of their own. Materials with defects will produce a magnetic field that is different from that of a reference material without defects and an appropriate detection instrument is required to determine these differences.

Sonics: In the use of ultrasonics, pulses of sound energy are transmitted through a couplant, such as oil or water, onto the metal surface where waves are generated. The reflected echoes are converted to electrical signals that can be interpreted to show the location of flaws or pits. Both contact and immersion methods are used. The test has good sensitivity and provides instantaneous information about the size and location of flaws. However, reference standards are required for comparison and training is needed to interpret the results properly.

An alternative approach is to use acoustic emissions in detecting flaws in metals. Imperfections, such as pits, generate high frequency emissions under thermal or mechanical stress. The frequency of emission and the number of occurrences per unit time determine the presence of defects.

Penetrants: Defects opening to the surface can be detected by the application of a penetrating liquid that subsequently exudes from the surface after the excess penetrant has been removed. Defects are located by spraying the surface with a developer that reacts with a dye in the penetrant, or the penetrant may contain a fluorescent material that is viewed under black light. The size of the defect is shown by the intensity of the colour and the rate of bleed-out. This technique provides only an approximation of the depth and size of pits.

However, none of these non-destructive test methods provide satisfactory detailed information about pitting. They can be used to locate pits and to provide some information about the size of pits, but they generally are not able to detect small pits, and confusion may arise in attempting to differentiate between pits and other surface blemishes. Most of these methods were developed to detect cracks or flaws in metals, but with more refined development they may become more applicable to pitting measurements.

STANDARDS FOR ASSESSING THE PITTING RESISTANCE AND THE EXTENT OF PITTING

1. ASTM G61-86 (re-approved 1993), Standard test method for conducting cyclic polarisation measurements for localized corrosion susceptibility of iron, nickel or cobalt based alloys.
2. ASTM G46-76 (re-approved 1986), Standard practice for examination and evaluation of pitting corrosion.
3. ASTM G59-97, Standard test method for conducting potentiodynamic polarization resistance measurements.
4. ASTM G3-89 (reapproved 1994), Standard practice for conventions applicable to electrochemical measurements in corrosion testing.
5. ASTM G109, Polarization resistance evaluating corrosion rate of metals.